

# PATENT APPLICATION

## POTENTIOMETRIC SENSOR FOR WELLBORE APPLICATIONS

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## Potentiometric Sensor for Wellbore Applications

The invention relates to a chemical sensor tool for use in downhole analyzing of fluids produced from subterranean formations. More specifically it relates to a potentiometric sensor for downhole pH and ion content analysis of effluents produced from subterranean formation

### BACKGROUND OF THE INVENTION

Analyzing samples representative of downhole fluids is an important aspect of determining the quality and economic value of a hydrocarbon formation.

Present day operations obtain an analysis of downhole fluids usually through wireline logging using a formation tester such as the MDT™ tool of Schlumberger Oilfield Services. However, more recently, it was suggested to analyze downhole fluids either through sensors permanently or quasi-permanently installed in a wellbore or as through sensor mounted on the drillstring. The latter method, if successful implemented, has the advantage of obtaining data while drilling, whereas the former installation could be part of a control system for wellbores and hydrocarbon production, therefrom.

To obtain an albeit crude estimate of the composition of downhole fluids, the MDT tools uses an optical probe to estimate the amount of hydrocarbons in the samples collected from the formation. Other sensors use resistivity measurements to discern various components of the formations fluids.

Particularly, knowledge of downhole formation (produced) water chemistry is needed to save costs and increase production at all stages of oil and gas exploration and production. The following applications are of interest:

- Prediction and assessment of mineral scale and corrosion;
- Strategy for downhole oil/water separation and water re-injection;

- 5 -Understanding of reservoir compartmentalization / flow units;
- Characterization of water break-through;
- Derivation of  $R_w$ .

10 Some chemical species dissolved in water (like, for example,  $Cl^-$  and  $Na^+$ ) do not change their concentration when removed to the surface either as a part of a flow through a well, or as a sample taken downhole. Consequently information about their quantities may be obtained from downhole samples and in some cases surface samples of a flow. However, some chemical species, 15 such as  $H^+$  ( $pH = -\log[\text{concentration of } H^+]$ )  $CO_2$ ,  $H_2S$  and water parameters, such as ORP (redox potential or Eh), do change significantly while trip to the surface. This change occurs mainly due to a huge difference in temperature and pressure between downhole and surface environment. In case of sampling, 20 this change may also happen due to degassing of a sample (seal failure), mineral precipitation in a sampling bottle, and (especially in case of  $H_2S$ ) - a chemical reaction with the sampling chamber. It should be stressed that pH,  $H_2S$ ,  $CO_2$ , and ORP are among the most critical parameters for corrosion and 25 scale assessment. Consequently it is of considerable importance to have their downhole values precisely known.

Hence, there is and will continue to be a demand for downhole chemical measurements. However, no downhole chemical 30 measurements actually performed in a oil and gas producing well have been reported so far.

To meet demand for chemical measurements of increasing accuracy, it may appear obvious to adapt chemical analysis tools known 35 from chemical laboratory practice to the hostile environment of

a subterranean borehole. Such known analysis tools include for example the various types of chromatography, electrochemical and spectral analysis. Particularly, the potentiometric method has been widely used for the measurements of water composition (pH, Eh, H<sub>2</sub>S, CO<sub>2</sub>, Na<sup>+</sup>, Cl<sup>-</sup> etc...) both in the laboratory and in the field of ground water quality control. However, so far the environmental conditions within a subterranean wellbore rendered attempts to perform such measurements under real hydrocarbon wellbore condition purely theoretical.

Among the known state of the art in the field of high temperature potentiometric are: Diakonov I.I., Pokrovski G.S., Schott J., Castet S., and Gout R. J.-C. "An experimental and computational study of sodium - aluminum complexing in crustal fluids", in: *Geochim. Cosmochim. Acta*, **60**(1996), 197-211 and Midgley D. "A review of pH measurement at high temperatures", in: *Talanta*, **37**(1990), 8, 767-781.

General downhole measurement tools for oilfield applications are known as such. Examples of such tools are found in the United States Patents Nos. 6,023,340; 5,517,024; and 5,351,532 or in the International Patent Application WO 99/00575. An example of a probe for potentiometric measurements of ground water reservoirs is published as: Solodov, I.N., Velichkin, V.I., Zotov, A.V. et al. "Distribution and Geochemistry of Contaminated Subsurface Waters in Fissured Volcanogenic Bed Rocks of the Lake Karachai Area, Chelyabinsk, Southern Urals" in: Lawrence Berkeley Laboratory Report 36780/UC-603(1994b), RAC-6, Ca, USA.

It is therefore an object of the present invention to provide apparatus and methods to perform potentiometric measurements in a subterranean wellbore for hydrocarbon exploration and production.

## SUMMARY OF THE INVENTION

The invention achieves its objects by providing a potentiometric sensor with at least one reference and one measuring electrode  
5 having a permanent aqueous contact between measuring and reference electrode. The contact is preferably ensured by discharging the internal solution from the reference electrode directly onto a measuring (ion-sensitive) membrane and protecting the reference junction of the reference electrode  
10 with water wet porous material, such as sintered glass.

In a preferred embodiment, the stability of a signal / electrode fouling can be checked by measuring a signal with and without an additional resistance.

A potentiometric technique can be applied for example as part of a production logging tool and open hole formation tester tool (Modular Dynamic Tester, MDT). In the latter case, the technique can provide a downhole real-time water sample validation or  
20 downhole pH and H<sub>2</sub>S measurements for prediction of mineral scale and corrosion assessment. A new gas sensing combination potentiometric sensor is also proposed for simultaneous detection of H<sub>2</sub>S and CO<sub>2</sub> partial pressures in any fluid (oil, gas, water).

25 These and other features of the invention, preferred embodiments and variants thereof, possible applications and advantages will become appreciated and understood by those skilled in the art from the following detailed description and drawings.

## BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 shows a schematic diagram of the main elements of a known potentiometric sensor;

FIG. 2 shows details of a reference electrode of a known potentiometric sensor;

FIG. 3 shows a schematic diagram of a downhole probe of a known potentiometric sensor;

FIG. 4 shows a schematic diagram of the main elements of an example of a potentiometric sensor in accordance with the present invention;

FIGS. 5A,B illustrate variants of a potentiometric sensor in accordance with the present invention;

FIG. 6 shows a self-discharging reference electrode for use as part of a potentiometric sensor in accordance with the present invention;

FIG. 7,8 illustrates further variants of discharging electrodes;

FIG. 9 illustrates a further variant of an analyzing tool as part of a permanently installed flow monitoring unit in a wellbore;

FIG. 10 shows a compact potentiometric probe of particular use for a downhole application, in accordance with the invention;

FIG. 11 shows a formation testing apparatus held on a wireline within a wellbore, in accordance with the invention;

FIG. 12 shows a wellbore and the lower part of a drill string including the bottom-hole-assembly, in accordance with the invention;

FIG. 13 shows a sensor located downstream of a venturi-type flowmeter, in accordance with the invention; and

FIG. 14 depicts an example of continuous measurement that has been performed in a shut oil producer, in accordance with the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The theory of potentiometry and its application to water measurements at ambient temperatures are well developed. The method is based on the measurement of electromotive force (e.m.f., or E) in a potentiometric cell which consists of measuring and reference electrodes (half-cells).

FIG. 1 shows the general components of a known potentiometric cell. A measuring electrode is inserted into a solution. This electrode consists of an internal half element (for example, Ag wire covered by an AgCl salt) in a solution of a fixed pH (for example, 0.1M HCl in some pH electrodes), and an ion-selective membrane (like glass  $H^+$  selective membrane in pH glass electrode). The reference electrode also contains an internal half-element (typically the same AgCl;Ag) inserted in a concentrated KCl (for example 3M) solution / gel saturated with  $Ag^+$ , which diffuses (or flows) through the reference (liquid) junction.

Details of the reference electrodes are shown in FIG. 2: A reference electrode contains an internal half-element (typically AgCl;Ag) inserted in a concentrated KCl (for example 3M) solution / gel saturated with  $Ag^+$ , which diffuses (or flows) through the reference (liquid) junction, thus maintaining electrical contact. The potential of this electrode is fixed at a constant temperature as chloride ion concentration inside is a constant. It is important that the membrane (RJ) should stay

intact (no clogging / fouling) and consequently (b) there should aqueous continuum between measuring and reference electrode.

The ion-selective electrode measures the potential that arises because of the difference in concentrations of a corresponding ion ( $H^+$  in case of pH) in the internal solution and in the measured solution. This potential is measured against the reference potential on the reference electrode, which is fixed because of a constant composition of a reference solution / gel (see FIG. 2). Electrodes may be separate (separate half cells), and combined into one ("combination electrode").

The measuring electrode has a special sensitive ion-selective membrane. The membrane potential is related to the activity (concentration) of a given ion in a solution. The reference electrode has a constant potential (see FIG. 2). The measured e.m.f. ( $E$ , potential difference) is an overall a function of the temperature and the activity of an  $i$ th ion, to which the measuring electrode is selective:

$$[1] \quad E = E^0 + (k \cdot T) \cdot \log(a_i),$$

where  $E$  is the measured electromotive force (e.m.f.) of the cell (all potentials are in V),  $a_i$  corresponds to the activity of the  $i$ th ion and is proportional to its concentration.  $E^0$  is the standard potential (at temperature  $T$ ) corresponding to the  $E$  value in a solution with the activity of  $i$ th ion equal to one. The term in parenthesis is a so-called Nernstian slope for the plot of  $E$  as a function of  $\log(a_i)$ . This slope (or the constant " $k$ ") together with the cell (electrode) constant ( $E^0$ ) is experimentally determined via a calibration procedure using standard solutions with known activities of  $i$ th ion. For good quality undamaged electrodes this slope should be very close to the theoretical one, equal to  $(R \cdot T / F \cdot z)$ , where  $F$  is the Faraday constant (23061 cal/mole),  $R$  is the gas constant (1.9872



cal/mole K),  $z_i$  is the charge of  $i$ th ion. The schematic design of a potentiometric cell is shown in FIG. 1 above. Note that potentiometric electrodes may be used as separate entities (separate, individual electrodes, or half-cells) or be assembled in a "combination" electrode (like very popular pH combination glass electrode).

In FIG. 3, there are schematically illustrated elements of a known downhole analyzing tool as used by Solodov et al (see background). Potentiometric electrodes are located at the bottom part of the probe and include those for pH, Eh (or ORP),  $\text{Ca}^{2+}$  (pCa),  $\text{Na}^+$  (pNa),  $\text{S}^{2-}$  (pS),  $\text{NH}_4^+$  (pNH<sub>4</sub>), and reference electrode (RE).  $\text{H}_2\text{S}$  partial pressure may be calculated from pH and pS readings.

In the follow major aspects of the invention are described in detail. These aspects cover three main areas:

- The adaptation of potentiometric method to measurements in oil/water mixtures including oil-continuous phase
- Use of the method in downhole tools
- Design of a new gas-sensing combination electrode for the simultaneous detection of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  partial pressures.

A first aspect relates to the adaptation of potentiometric method to measurements in oil/water mixtures including oil-continuous phase.

Such Potentiometric measurements are feasible under two conditions:

Firstly, the membranes (measuring and RJ) should stay intact without clogging or fouling. The second condition is to provide an aqueous continuum between measuring and reference electrode.

It was found that glass and silver sulfide membranes are not prone to immediate fouling by oil and its components.

Consequently, in this invention devices are used which eliminate fouling or clogging of the reference junction (RJ) of the

5 reference electrode. Simultaneously with eliminating RJ fouling these devices help to establish a stable aqueous contact between measuring and reference electrodes thus allowing stable measurements in oil continuous phase. Some of the proposed devices also decrease fouling of the ion-sensitive membranes of  
10 the measuring electrodes.

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All of the above is achieved by using a passive water-wet protection layer on the reference junction, The protection layer is manufactured from special porous water wet materials (for  
5 example, a sintered glass frit). When used in combination electrodes with glass/silver sulfide (or similar) membranes which are not very prone to fouling, this device enables measurements until glass membrane fouling occurs as it does not protect the measuring electrode.

By adding an induced discharge of the reference solution / gel directly onto measuring membrane of the measuring (ion-selective) electrode, a closed electrical circuit is created even in water-in-oil emulsions. This procedure may be applied in  
25 conjunction with the use of the above-described water-wet protective cap. In combination, discharge and cap allow measurements in oil continuous phase (maintaining water layer on measuring surface and RJ) and simultaneous membrane cleaning by an induced discharge of reference fluid. This reference fluid  
30 may also clean the membrane of the measuring electrode.

FIG. 4 shows a combination pH electrode consists of pH glass electrode and an enveloping reference electrode. Reference electrode has a protective water-wet cap on the reference  
35 junction. The cap is made from sintered glass. This material may

or may not itself be saturated with the reference gel. A protective water-wet cap ensures a constant presence of a water continuous layer on the surface of the cap and consequently a closed circuit with the measuring glass pH membrane. KCl gel / solution either diffuses through the cap, or is pushed through via various means to ensure electrical contact. The water present in water-in-oil emulsion exchanges with the water in a surface layer on top of this sensor. Consequently, the measurement accounts for any change in the effluent passing the sensor (see Fig. 4).

In FIGS. 5A and 5B there are shown two variants having a separate reference and measuring electrodes. The measuring glass membrane of pH electrode is water-wet. An electrical contact in water-in-oil emulsions is assured via a direct discharge of a reference solution / gel onto a surface of the measuring membrane. This is achieved either via diffusion (or induced flow) through a water -wet protective cap (e.g. a sintered glass disc) (FIG. 5A) or through a capillary contact (FIG. 5B). The reference solution / gel may be pushed out from the reference electrode via various means.

Direct discharge of reference solution / gel is achieved via pushing it out of the reference electrode with the help of

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- a piston;
- a load, placed on top of an inflatable chamber filled with reference solution;
- a buoyancy system, where a floating chamber is filled with a light gas is placed underneath a flexible chamber filled with the reference solution. Consequently, this floating chamber exert a pressure onto a flexible tank with a reference fluid; or variants or combinations thereof.

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A self-discharging type reference electrode is shown in FIG. 6. The reference electrode may be filled with aqueous solution (usually KCl), gel, or solid electrolyte (or it may contain a solid micro-porous matter saturated with an aqueous solution or gel). The induced discharge of the reference electrolyte establishes an aqueous electrical contact with the measuring electrode. The discharge itself is achieved using a self-compressing deformable reference electrode (2). A flexible bag (2) is charged in a stretched state. The bag is then closed by a gland (3) having a central passage filed with a micro-porous medium (4). The elastic force compresses the bag and pushes solution out through the medium(4). In this design, neither the rate nor time of solution outflow may be controlled.

Further examples of discharge type reference electrodes are shown in FIGs. 7 and 8.

The electrode of FIG.7 comprises a piston exerting a pressure onto an inner chamber of the reference electrode. The chamber is filled with the reference aqueous solution or gel. The porous water-wet material of the cap ensures an electrical contact to the pH sensing membranes. In operation the piston can be driven by an external motor or hydraulic system.

In the variant of FIG. 8, a gas-filled chamber replaces the piston of FIG. 7. The reference solution is stored in a flexible bag.

The above sensor design can be improved by an internal measurement against a known resistor as shown in FIG. 9. An additional resistance "R" placed between the measuring and reference electrodes will enable a check for electrical contact quality to be carried out. The electrode pair may be regarded as a battery with its internal resistance "r". This internal resistance is caused by electrodes and the measuring solution.

The resistance of the glass electrodes is very high ( $>10$  MOhm), whereas the resistance of the pure aqueous solutions (no oil) and the reference electrode (Ag, AgCl) is very small compared to the resistance of the glass electrodes. The resistance of oil may be comparable to that of the glass electrodes. Consequently, when the space between the electrodes fills with oil, the oil forms a fouling film on their surfaces, the overall resistance of a cell increases and the signal changes. Measuring this cell resistance with the help of a reference measurement performed employing an additional resistance "R" indicates the quality of the electrical contact. A condition for a good electrically conductive circuit is a stable, constant voltage drop when the additional resistance is switched on.

A compact potentiometric probe of particular use for a downhole application is shown in FIG. 10. The probe may be placed inside the module body (shown) or inside a sampling bottle. A system of valves, flow lines and additional chambers (not shown) ensures the contact of the probe's sensors with the sample effluent. This system may also supply calibration and cleaning solutions downhole.

In FIGs. 11 - 13 the sensor is shown in various possible downhole applications.

In FIG. 11, there is shown a formation testing apparatus **110** held on a wireline **112** within a wellbore **114**. The apparatus **110** is a well-known modular dynamic tester (MDT, Mark of Schlumberger) as described in the co-owned U.S. Pat. No. 3,859,851 to Urbanosky U.S. Pat. No. 3,780,575 to Urbanosky and Pat. No. 4,994,671 to Safinya et al., with this known tester being modified by introduction of a potentiometric analyzing tool **116** as described in detail above. The modular dynamics tester comprises body **120** approximately 30m long and containing a main flowline bus or conduit **122**. The analysing tool **116**

communicates with the flowline **122** via opening **117**. In addition to the novel sensor system **116**, the testing apparatus comprises an optical fluid analyser **130** within the lower part of the flowline **122**. The flow through the flowline **122** is driven by means of a pump **132** located towards the upper end of the flowline **122**. Hydraulic arms **134** and counterarms **135** are attached external to the body **120** and carry a sample probe tip **136** for sampling fluid. The base of the probing tip **136** is isolated from the wellbore **114** by an o-ring **140**, or other sealing devices (packers).

Before completion of a well, the modular dynamics tester is lowered into the well on the wireline **112**. After reaching a target depth, i.e., the layer of the formation which is to be sampled (here: **142**), the hydraulic arms **134** are extended to engage the sample probe tip **136** with the formation. The o-ring **140** at the base of the sample probe **136** forms a seal between the side of the wellbore **144** and the formation **142** into which the probe **136** is inserted and prevents the sample probe **136** from acquiring fluid directly from the borehole **114**.

Once the sample probe **136** is inserted into the formation **142**, an electrical signal is passed down the wireline **112** from the surface so as to start the pump **132** and the sensor systems **116** and **130** to begin sampling of a sample of fluid from the formation **142**. The potentiometric detector **116** is adapted to measure the pH and ion-content of the formation effluent.

A bottle (not shown) within the MDT tool may be filled initially with a calibration solution to ensure in-situ (downhole) calibration of sensors. The MDT module may also contain a tank with a greater volume of calibration solution and/or of cleaning solution which may periodically be pumped through the sensor volume for cleaning and re-calibration purposes.

Potentiometric probes in an MDT-type downhole tool may be used for the absolute measurements of downhole parameters which significantly differ from those measured in samples on the surface (such as pH, Eh, dissolved H<sub>2</sub>S, CO<sub>2</sub>). This correction of surface values are important for water chemistry model validation.

A further possible application of the novel sensor and separation system is in the field of measurement-while-drilling (MWD). The principle of MWD measurements is known and disclosed in a vast amount of literature, including for example United States Patent No. 5,445,228, entitled "Method and apparatus for formation sampling during the drilling of a hydrocarbon well".

In FIG. 12, there is shown a wellbore **211** and the lower part of a drill string **212** including the bottom-hole-assembly (BHA) **210**. The BHA carries at its apex the drill bit **213**. It includes further drill collars that are used to mount additional equipment such as a telemetry sub **214** and a sensor sub **215**. The telemetry sub provides a telemetry link to the surface, for example via mud-pulse telemetry. The sensor sub includes the novel potentiometric analyzing unit **216** as described above. The analyzing unit **216** collects fluids from the wellbore via a small recess **217** protected from debris and other particles by a metal mesh.

During drilling operation wellbore fluid enters the recess **217** and is subsequently analyzed using sensor unit **216**. The results are transmitted from the data acquisition unit to the telemetry unit **214**, converted into telemetry signals and transmitted to the surface.

A third application is illustrated in FIG. 13. It shows a venturi-type flowmeter **310**, as well known in the industry and

described for example in the United States Patent No. 5,736,650. Mounted on production tubing or casing **312**, the flowmeter is installed at a location within the well **311** with a wired connection **313** to the surface following known procedures as disclosed for example in the United States Patent No. 5,829,520.

The flowmeter consists essentially of a constriction or throat **314** and two pressure taps **318**, **319** located conventionally at the entrance and the position of maximum constriction, respectively. Usually the venturi is combined with a densiometer **315** located further up- or downstream.

The novel potentiometric analyzing unit **316** is preferably located downstream from the venturi to take advantage of the mixing effect the venturi has on the flow. A recess **317** protected by a metal mesh provides an inlet to the unit.

During production wellbore fluid enters the recess **317** and is subsequently analyzed using sensor unit **316**. The results are transmitted from the data acquisition unit to the surface via wires **313**.

The above system allows continuous measurements in a water-in-oil emulsion up to 90 vol% of crude oil. An exemplary measurement has been performed in a shut oil producer and is depicted in FIG 14.

The logs #1 and #2 were recorded using a potentiometric probe as described in FIG. 3. The recording took place after pulling out tubing in a cased well (ID casing 139.7 mm) in the Kazanskoe oilfield, Suhodol area, 120 km north-east from Samara city, Russia.

Log#1 was recorded with separated pH and reference electrodes without water-wet connection between the electrodes. No signal



was recorded in oil layer (700-870m) due to the absence of an electrical contact. In the underlying brine a stable reproducible signal was recorded. This is due the water-wet surface of a glass pH electrode (no oil fouling) and continuous induced discharge of the reference KCl solution out of the reference electrode (no fouling of the reference junction.

Log#2 was recorded with a capillary contact between the reference electrode and the pH glass membrane ("connector"). KCl solution was continuously pushed out of the reference. This ensured a direct discharge of KCl liquid onto glass membrane, i.e. a stable electrical contact in oil. Note that the presence of the connector resulted in reasonable pH values in a layer of nearly pure oil (700-870 m) (red and blue lines). These values roughly correspond to the pH of brine just below oil layer. Note also the good agreement between upwards and downwards logs recorded at different speeds in brine.

The stability of a signal / electrode fouling was checked via measuring a signal with and without an additional resistance as a function of time (see Fig.9).

Design of new electrodes and use of new combinations of potentiometric electrodes in oil-water mixtures

A new gas sensing combination is proposed which allows simultaneous determination of partial pressures of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  in any phase (oil, gas, water). This is a modification of existing gas-sensing combinations. The novelty is that the present invention proposes the use of three electrodes (pH, pS, and reference) in one sensor in order to obtain simultaneously the partial pressures for the above two gases.

Various embodiments of the invention have been described. The descriptions are intended to be illustrative of the present

invention. It will be apparent to those skilled in the art that modifications may be made to the invention as described without departing from the scope of the claims set out below.